FORMS OF CADMIUM IN SANDY SOILS AFTER AMENDMENT WITH SOILS OF HIGHER FIXING CAPACITY

S. S. Mann & G. S. P. Ritchie

Abstract

Most of the Cd applied through phosphatic fertilizers in sandy soils tends to stay in mobile forms (soluble or exchangeable) and hence the risk of it leaching to underground water or its uptake by plants is higher. A sequential extraction procedure was used to assess the efficacy of amending materials (soils containing inorganic or organic adsorption components) on the re-distribution of forms of Cd in a sandy soil.

Amendment of the sandy soil with each of the three soils (yellow earth, lateritic podzolic and peaty sand) was generally effective in altering the more mobile or available forms of Cd to immobile or unavailable forms. The extent of alteration varied with the type of component present in the amendment soil, pH and the rate of Cd addition. The yellow earth was more effective at pH 7, whereas the peaty sand was equally effective at both pH 4 and 7 in altering the mobile to immobile forms. The lateritic podzolic soil was the least effective of the soils used at any of the pH values.

INTRODUCTION

Cadmium (Cd) is potentially a toxic heavy metal and occurs widely in nature in small amounts. It is a common impurity in phosphorus fertilizers (Williams and David, 1973; Mann, 1989), so the Cd content of agricultural soils can increase due to the application of phosphatic fertilizers and can ultimately increase the concentration of Cd in the food crops grown on them.

Sandy soils cover a large area of the world and are used for agricultural production in many areas (FAO-UNESCO, 1974). In Australia, such soils occupy approximately 18 million ha excluding the desert regions. Phosphorus is commonly deficient in Western Australian, sandy soils (Ozanne and Shaw, 1967) where high rates of phosphorus fertilizer are required, particularly for horticultural crops. Much of the Cd applied through phosphatic fertilizers to sandy soils remains in soluble or exchangeable forms due to a lack of adsorption sites on soil surfaces (Cox *et al.*, 1984; Mann and Ritchie, 1993). Consequently there is a greater risk of Cd being either taken up by crops or leached to ground water in sandy soils (Emmerich *et al.*, 1982).

Organic matter, hydrous oxides of iron, aluminium and manganese and clay minerals are the major components of the soil that may contribute to the retention of Cd in non-mobile or unavailable forms (Sposito and Page, 1985; Van Riemsdijk *et al.*, 1990). The amendment of sandy soils with material containing high amounts of these components may reduce the risk of Cd leaching or its uptake by plants (Verloo and Willaert, 1990). The application of inorganic materials such as mining wastes, e.g. bauxite residues, synthetic rutile wastes (Tacey *et al.*, 1984; Vlahos *et al.*, 1989) and organic wastes, e.g. sewage sludge, organic manures, etc. (Emmerich *et al.*, 1982; Neal and Sposito, 1986) have been used to reduce the leaching of heavy metals from soils. A possible limitation with these materials is that they may themselves contain Cd or other heavy metals, and therefore increase the burden of Cd in the sandy soils and leave Cd in leachable and plant available forms (Soon and Bates, 1982). An alternative approach is to amend sandy soils with soils that are rich in clay, hydrous oxides or organic matter, and are free from heavy metal contamination.

Cadmium can exist in soils in several different forms depending upon the type and quantity of soil components, pH and the amount of Cd that has been applied (Christensen, 1984; Brummer, 1986; Mann and Ritchie, 1993). The incorporation into a sandy soil of soil components that can fix Cd could alter the equilibrium between existing forms of Cd, and therefore reduce its solubility.

The objective of this study was to investigate the changes in the forms of Cd in a sandy soil after addition of soils containing inorganic or organic adsorption sites for Cd.

MATERIALS AND METHODS

Cadmium was sequentially extracted from a siliceous sand after mixing with three soils at two pH values and in the presence of four rates of Cd addition.

Soils

The sandy soil (pH 5·75) was collected from a siliceous sand, SS (Northcote classification: Uc 2.22; Northcote, 1974). The 'amendment' soils were a yellow earth, YE (Northcote classification: Uc 1.22), a lateritic podzolic, LP (Northcote classification: Uc 5.51) and a peaty sand, PS (Northcote classification: Uc 2.33). The yellow earth (pH 5·40) and lateritic podzolic (pH 3·74) soils were

Table 1. Details of soil mixtures, some of their properties and codes used in figures

Soils in mixture	pH	Proportions (%)	Total Cd ($\mu g\ g^{-1}$)	Organic carbon (%)	Main adsorption components	Codes for figures
Siliceous sand	4	100/0	<0·01	0·12	Quartz	1–4
Siliceous sand	7	100/0	<0·01	0·12		2–7
Yellow earth/siliceous sand	4	50/50	0·03	0·15		3–4
Yellow earth/siliceous sand	4	100/0	0·07	0·31	Geothite and kaolinite	5–4
Yellow earth/siliceous sand	7	50/50	0·03	0·15		4–7
Yellow earth/siliceous sand	7	100/0	0·07	0·31		6–7
Lateritic podzolic/siliceous sand	4	50/50	0·06	0·15		7–4
Lateritic podzolic/siliceous sand	4	100/0	0·14	0·30	Kaolinite	9–4
Lateritic podzolic/siliceous sand	7	50/50	0·06	0·15		8–7
Lateritic podzolic/siliceous sand	7	100/0	0·14	0·30		10–7
Peaty sand/siliceous sand	4	50/50	<0·01	1·57		11–4
Peaty sand/siliceous sand	4	75/25	<0·01	2·09		13–4
Peaty sand/siliceous sand	4	100/0	<0·01	3·14	Organic matter	15–4
Peaty sand/siliceous sand	7	50/50	<0·01	1·57		12–7
Peaty sand/siliceous sand	7	75/25	<0·01	2·09		14–7
Peaty sand/siliceous sand	7	100/0	<0·01	3·14		16–7

collected from a depth of 25–45 cm and were mainly dominated by goethite and kaolinite, respectively. The peaty sand (pH 4·04) was collected from the 0–20 cm layer after removing the vegetation and clearing the debris. Organic matter was the main adsorption component of this soil. Some properties of the soils are given in Table 1.

Preparation of soil mixtures

A portion (200 g) of each amendment soil (yellow earth, lateritic podzolic and peaty sand), adjusted to pH 4 and 7 as described by Mann and Ritchie (1993), were taken and mixed with the siliceous sand (also adjusted to pH 4 and 7) in different ratios to obtain sixteen soil mixtures (Table 1). The soil mixtures were brought to their field capacities by adding $Cd(NO_3)_2$ that contained sufficient Cd to amend the mixtures with 0, 0·8 and 10 μg Cd g^{-1} soil. After thorough mixing, the soil mixtures were incubated at 40 ± 1°C for 24 h, which was sufficient time for >90% of the applied Cd to be adsorbed (Mann and Ritchie, 1993).

Extraction of forms of Cd

Triplicate subsamples of each mixture were extracted by a sequential extraction scheme (Mann and Ritchie, 1993) to estimate the different forms of Cd present, which will be operationally defined as soluble (0·005 M KCl), exchangeable (0·1 M $BaCl_2$), bound to organic matter (5·3% NaOCl), bound to hydrous oxides (ammonium oxalate solution, i.e. AO) and residual (concentrated acids) forms of Cd. In reality, this is an approximation because each reagent will not necessarily extract one specific form.

Cadmium analysis

Cadmium extracted by different solutions was analysed by atomic absorption spectroscopy using either a flame-AAS or a graphite furnace (Mann and Ritchie, 1993). The accuracy of the methods for analysing Cd in different solutions was tested by Mann (1993).

Data analysis

Standard errors of the triplicate samples were calculated and are shown as error bars in all figures.

RESULTS

Native Cd

No Cd was extracted from the siliceous sand or the mixtures containing the peaty sand (<10 ng g^{-1} soil) at either pH value in any of the extracting solutions. All of the native Cd was extracted as residual Cd from the mixtures of the yellow earth and the lateritic podzolic soils at pH 4 and 7 (data not shown).

Added Cd

The addition of the amendment soils had a marked effect on the forms of added Cd in the siliceous sand, when Cd was applied at different rates, and the effect varied with pH. The amount of Cd and the percentage of applied Cd in each form varied with the treatments in a similar manner.

Siliceous sand (100%)

In the 100% siliceous sand, the added Cd was almost wholly recovered in the forms of either Cd-KCl (soluble) or Cd-$BaCl_2$ (exchangeable). The highest recoveries of added Cd, as Cd-NaOCl (bound to organic matter) and in Cd-acid extractable (residual forms) were 5 and 4% respectively at pH 7 and 10 $\mu g\ g^{-1}$ Cd added. At pH 4, the recoveries in these fractions were <2% at all the Cd application rates. The recovery of added Cd in Cd-AO (bound to oxide) was <1%.

The pH of the sand and the rate of Cd addition had a large influence on the relative proportions of Cd-KCl and Cd-$BaCl_2$. At pH 4, at either Cd addition rate, 60–70% of added Cd was in the Cd-KCl form, the rest being nearly all as Cd-$BaCl_2$. At pH 7 and with 0·8 $\mu g\ g^{-1}$ added Cd, 40% was present as Cd-KCl and 60% as Cd-$BaCl_2$; for the 10 $\mu g\ g^{-1}$ Cd rate, the respective proportions were 15 and 80%.

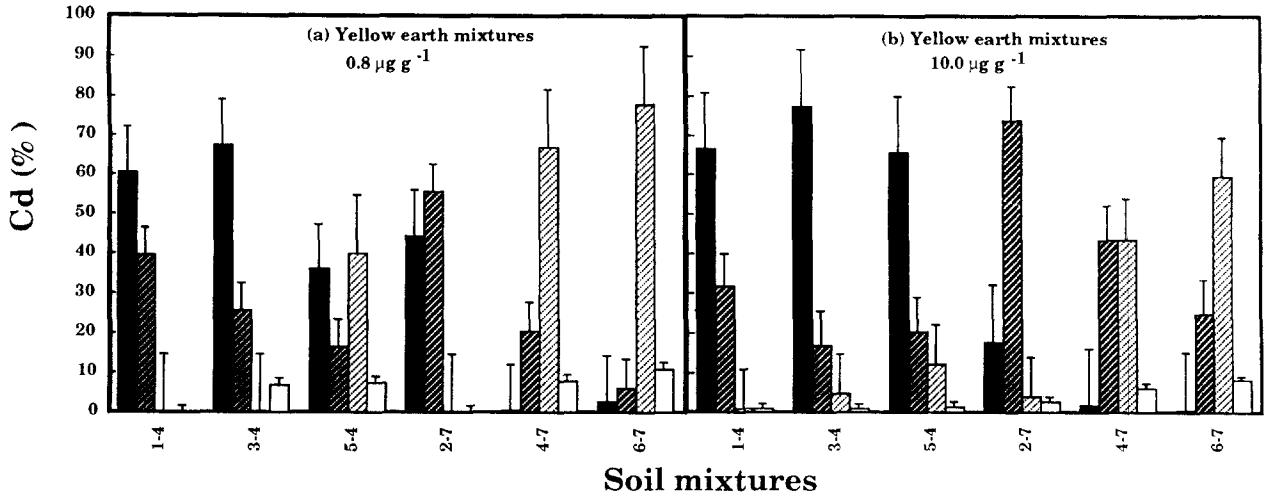

Fig. 1. The relationship of soil components in yellow earth soil mixtures at: (a) 0·8 μg Cd g^{-1}; (b) 10 μg g^{-1} on soluble (■), exchangeable (▨), Cd bound to oxides (▩) and residual Cd (□) after mixing with siliceous sand. Vertical bar denotes the standard errors.

Yellow earth soil mixtures

At both application rates of Cd and at pH 4, there was no difference between the %Cd-KCl in the 50% yellow earth mixture and the siliceous sand (Figs 1(a) and 1(b)). At pH 7, a large decrease in Cd-KCl (20–40%) was noticed. The extent of the decrease was less at the higher Cd application rate (Figs 1(a) and 1(b)).

The percentage of Cd found in each extract was compared with that predicted by the equation $(xZ_1 + yZ_2)10^{-2}$. Respectively, x and y were the percentage Cd found in the siliceous sand and in each component separately, and Z_1 and Z_2 were the respective proportions in which the siliceous sand and a component were mixed. The equation estimates the percentage Cd that would be found in each extract if no redistribution of Cd forms had occurred. The Cd-KCl in the 50% mixture was greater than the predicted value at pH 4 and less at pH 7 (Table 2).

The Cd-$BaCl_2$ decreased with increase in the yellow earth in a mixture at all the Cd rates and at both pH values (Figs 1(a) and 1(b)). The extent of the decrease in Cd-$BaCl_2$ declined with increasing Cd addition at both the pH values. At pH 4, the Cd-$BaCl_2$ decreased by almost 15% at both rates of Cd application when the mixture contained 50% yellow earth; at pH 7 the decrease was >35% (Figs 1(a) and 1(b)). The Cd-$BaCl_2$ at both the pH values in the 50% mixtures was less than the predicted amount at all the rates of Cd application (Table 2).

The NaOCl solution did not extract Cd from any of the mixtures at pH 4 at any of the rates of Cd application. At pH 7, this fraction was very small (<5%); a slight increase occurred as the amount of yellow earth in a mixture increased and as the rate of Cd addition increased (data not shown).

The Cd-AO increased with an increase in the yellow earth in a mixture at both pH values and at all the rates of Cd addition (Figs 1(a) and 1(b)). The relative increase in Cd-AO lessened with the rate of Cd addition at both pH values (Figs 1(a) and 1(b)). At pH 7, the amount of Cd-AO was almost nil in the 0% yellow earth mixture, and increased to nearly 70 and 45% in

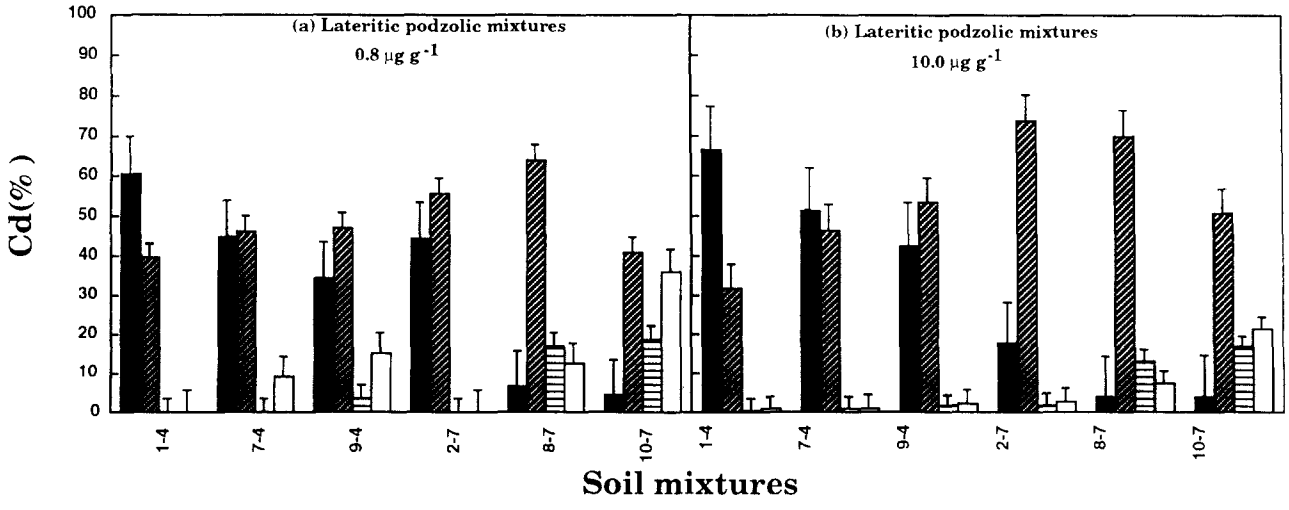

Fig. 2. The relationship of soil components in lateritic podzolic soil mixtures at: (a) 0·8 μg Cd g^{-1}; (b) 10 μg g^{-1} on soluble (■), exchangeable (▨), Cd bound to organic matter (▤) and residual Cd (□) after mixing with siliceous sand. Vertical bar denotes the standard errors.

Table 2. Cd (%) found and predicted in different soil mixtures

Mixture (%)	pH	Cd addition ($\mu g\ g^{-1}$)	Cd-KCl (%)		Cd-$BaCl_2$ (%)		Cd-NaOCl (%)		Cd-amm.Ox. (%)		Cd-residual (%)	
			Found	Predicted	Found	Predicted	Found	Predicted	Found	Predicted	Found	Predicted
Yellow earth	4	0·8	67·5	48·3	25·5	27·9	<0·1	<0·1	<0·1	20·0	7·0	3·7
(50%)		10	77·2	65·4	17·1	26·0	0·3	0·5	4·6	6·5	0·8	1·1
	7	0·8	0·6	24·0	20·6	30·9	4·0	1·1	67·0	39·0	7·8	5·3
		10	1·7	10·2	43·7	49·3	5·0	4·5	43·7	31·6	6·0	5·4
Lateritic Podzolic	4	0·8	44·6	47·5	46·3	43·3	<0·1	1·8	<0·1	<0·1	9·1	7·5
(50%)		10	51·5	54·6	46·6	42·4	0·9	0·9	<0·1	0·4	1·0	1·6
	7	0·8	6·7	24·4	64·1	48·2	16·8	9·3	<0·1	<0·1	12·5	18·1
		10	3·8	10·7	70·0	62·3	13·2	9·3	5·6	5·6	7·4	12·0
Peaty sand	4	0·8	10·1	30·8	51·0	56·3	36·5	13·0	2·5	<0·1	<0·1	<0·1
(50%)		10	9·6	33·8	53·9	50·8	31·2	12·2	4·8	2·4	0·4	0·8
	7	0·8	30·9	27·2	22·1	35·1	41·6	35·3	5·4	2·4	<0·1	<0·1
		10	22·1	17·5	15·9	45·5	54·5	29·8	6·4	5·3	0·9	1·9
Peaty sand	4	0·8	3·4	15·9	61·1	64·7	33·0	19·4	2·5	<0·1	<0·1	<0·1
(75%)		10	2·0	17·5	62·6	60·5	30·1	18·1	4·7	3·2	0·6	0·8
	7	0·8	23·0	18·6	10·0	24·9	58·8	52·9	7·0	3·5	1·2	<0·1
		10	19·1	17·4	10·3	31·4	62·4	43·8	6·7	6·0	1·5	1·5

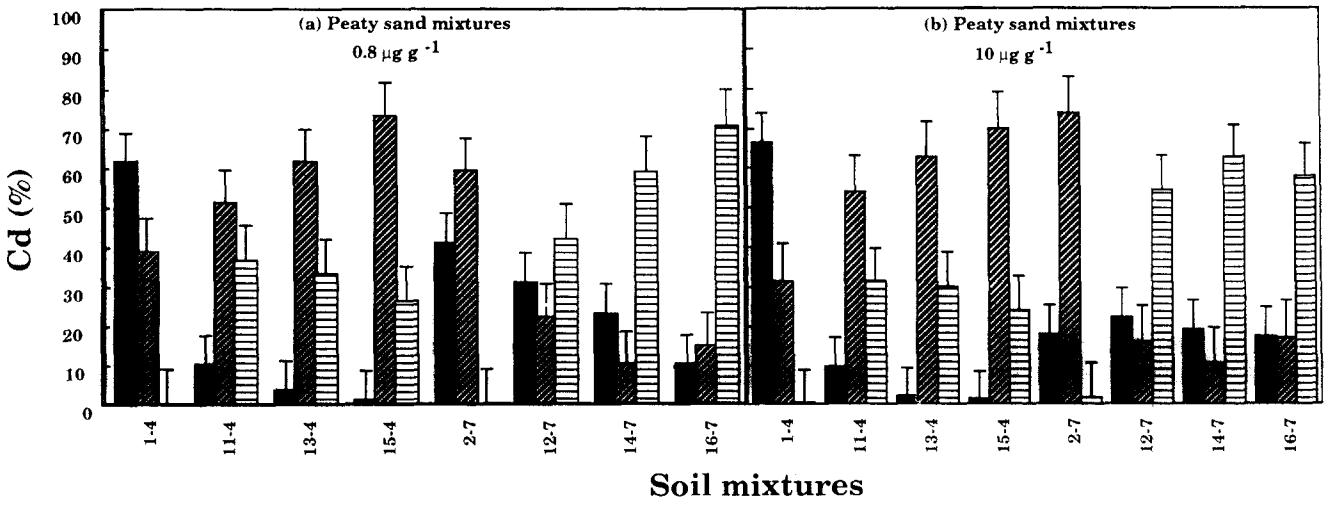

Fig. 3. The relationship of soil components in peaty sand soil mixtures at: (a) 0·8 μg Cd g^{-1}; (b) 10 μg g^{-1} on soluble (■), exchangeable (▨) and Cd bound to organic matter (▤) after mixing with siliceous sand. Vertical bar denotes the standard errors.

the 50% yellow earth mixtures at 0·8 and 10 μg g^{-1} Cd application rates respectively (Figs 1(a) and 1(b)). In contrast, at pH 4 there was no change in the amount of Cd-AO when the yellow earth content increased to 50% in the mixture. The Cd-AO at pH 4 was less than the predicted value in the 50% mixture, whereas at pH 7 the Cd-AO was more than the predicted value (Table 2).

Acid extractable Cd at both pH values was a small fraction (<10%) of the total Cd applied to all the soil mixtures at all the rates of Cd application (Figs 1(a) and 1(b)). A slight increase in Cd-acid extractable was observed with an increase in yellow earth in a mixture at both pH values. The increase was greatest at pH 7 and with the higher rate of Cd addition (Figs 1(a) and 1(b)). The Cd-acid extractable differed slightly from that predicted in the 50% mixtures at both pH values (Table 2).

Lateritic podzolic soil mixtures

At both pH values and at all the rates of Cd addition, the Cd-KCl tended to be lower in the 50% mixture than in the siliceous sand (Figs 2(a) and 2(b)). The decrease in %Cd-KCl was greater at pH 7 than at pH 4, and smaller at the higher rate of Cd addition. At pH 7 and 0·8 μg g^{-1} Cd addition, the decrease in Cd-KCl was almost 40%, whereas at pH 4 the decrease was approximately 15% (Fig. 2(a)). The Cd-KCl in the 50% mixture at pH 4 was very similar to that predicted; at pH 7 it was less than the predicted value at all the rates of Cd application (Table 2).

The Cd-$BaCl_2$ was 30–80% of the added Cd at both pH values and at all the rates of Cd addition (Figs 2(a) and 2(b)). At pH 4, mixing 50% of the lateritic podzolic soil with the siliceous sand slightly increased the Cd-$BaCl_2$ at all the rates of Cd addition. At pH 7, the Cd-$BaCl_2$ increased slightly at 0·8 μg g^{-1} and decreased slightly at 10 μg g^{-1} Cd addition (Figs 2(a) and 2(b)). The Cd-$BaCl_2$ found in the 50% mixture was slightly higher than predicted at both pH values; however at pH 7, the difference in the amounts found and that predicted was greater (8–16%) in comparison to the difference at pH 4, i.e. < 5% (Table 2).

At pH 4, the Cd-NaOCl was a negligible fraction (< 5%) in all the soil mixtures at all the rates of Cd addition (Figs 2(a) and 2(b)). At pH 7, the Cd-NaOCl slightly increased (15–20%) when the siliceous sand was mixed with 50% of the lateritic podzolic soil irrespective of the rate of Cd application (Figs 2(a) and 2(b)). The Cd-NaOCl found at pH 7 was more than predicted in the 50% mixture (Table 2).

The Cd-AO was almost a negligible fraction at pH 4 (< 2%) and was very small (≈ 5%) at pH 7 in the 50 : 50 mixtures at all the rates of Cd application (data not shown).

At both pH values and at all the rates of Cd addition, the Cd-acid extractable increased when the lateritic podzolic soil was mixed with the siliceous sand (Figs 2(a) and 2(b)). The extent of the increase at both pH values declined with the rate of Cd addition (Figs 2(a) and 2(b)). The Cd-acid extractable found in the 50% mixture and that which was predicted were similar at pH 4, whereas at pH 7 it was slightly less than predicted (Table 2).

Peaty sand soil mixtures

The Cd-KCl decreased markedly with an increase in the peaty sand content in the soil mixture at both pH values, except at pH 7 when Cd was applied at a rate of 10 μg g^{-1} (Figs 3(a) and 2(b)). At pH 4, the Cd-KCl was 60% in mixtures containing no peaty sand and decreased to approximately 10% when the amount of peaty sand in the mixture increased to 50% and was < 5% in the mixture containing 75% peaty sand (Figs 3(a) and 3(b)). At pH 7, the Cd-KCl decreased slightly (≈ 10%) at the lower rate of Cd application (0·8 μg g^{-1}), but at the higher rate (10 μg g^{-1}) of Cd addition there was no change when the peaty sand increased from 0 to 50% in the soil mixture. At pH 4, the Cd-KCl found in the 50 and 75% mixtures was less than that predicted at both rates of Cd application, whereas at pH 7 the amounts found and those predicted were similar (Table 2).

The Cd-$BaCl_2$ increased linearly at pH 4 with increasing percentage of peaty sand in a mixture at all the rates of Cd application, whereas at pH 7 this fraction decreased with increasing peaty sand content in the soil mixture (Fig 3(a) and 3(b)). At pH 7, the maximum decrease in Cd-$BaCl_2$ was observed when the peaty sand in the mixture increased from 0 to 50% at all rates of Cd application. At pH 4, the Cd-$BaCl_2$ found in the 50 and 75% mixtures was almost the same as predicted, whereas at pH 7 it was less than predicted in the mixtures at all rates of Cd application (Table 2).

The Cd-NaOCl tended to increase with increasing percentage of peaty sand in a mixture at pH 7 at all rates of Cd addition (Figs 3(a) and 3(b)). At pH 4, this fraction increased from 0 to >30% when the peaty sand in a mixture increased from 0 to 50%. However, no further increase was observed with additional peaty sand in the soil mixture. In contrast, at pH 7, the Cd-NaOCl increased from 0 to >40% with the addition of 50% peaty sand, and there was a further increase when the peaty sand in the mixture increased to 75% (Figs 3(a) and 3(b)). The extent of the increase was less at the higher rate of Cd addition. The Cd-NaOCl found in the 50 and 75% mixtures was more than predicted at both pH values and at all rates of Cd addition (Table 2).

The Cd in the ammonium oxalate and the acid extracts was a very minor fraction (<7%) in all the peaty sand mixtures at both pH values (data not shown).

DISCUSSION

Amendment of the siliceous sand with each of the three soils was generally effective in changing the mobile or available forms of Cd to immobile or unavailable forms. The extent of transformation varied with the type of adsorption component present in the amendment soil, pH and the rate of Cd application. Soluble and exchangeable forms of Cd (considered the most labile or available forms for leaching and plant uptake; Harrison *et al.*, 1981; Soon and Bates, 1982; Hickey and Kittrick, 1984) decreased in the soil mixtures, whereas Cd bound by organic matter and hydrous oxides (less-labile or less available forms) increased when the siliceous sand was amended with the yellow earth, lateritic podzolic or peaty sand.

The yellow earth and peaty sand were generally more effective than the lateritic podzolic soil. The effects of pH and rate of Cd addition in transforming Cd were greater in the yellow earth mixtures than when the peaty sand was used. The lateritic podzolic soil was not as effective in amending material as the other two soils at either of the pH values.

The extent to which leaching or uptake were reduced by the amendment soils could not be predicted directly from the equation used for estimating the amount of Cd found in each form. Each soil could be considered effective at amending the siliceous sand if (i) the amounts of Cd found in soluble plus exchangeable form was less than the predicted value and (ii) the amounts of Cd bound to organic matter, hydrous oxides or in the residual form were greater than the corresponding predicted values for each of those forms. For example, without the amendment, >95% of the Cd in the siliceous sand was present in mobile or available forms. When the siliceous sand was amended with the yellow earth, the soluble form of Cd at pH 4 was greater than predicted (Table 2), presumably because of a lack of sites. At pH 7, the actual amount of soluble Cd was less than the predicted value, whereas Cd bound to oxides was more than the predicted value, suggesting that enough adsorption sites were present to transform the soluble Cd originating from the siliceous sand (Table 2). The extent of the transformation at pH 7 depended upon the rate of Cd application. At 0·8 $\mu g\ g^{-1}$ of Cd addition, more than 70% of the Cd was retained in immobile or unavailable forms, in comparison to 45% at 10 $\mu g\ g^{-1}$.

The addition of the peaty sand to the siliceous sand, to achieve a 50% peaty sand mixture at pH 4, resulted in smaller amounts of soluble Cd than predicted and larger amounts bound to organic matter than predicted (Table 2). In this instance, there were sufficient sites for nearly 30–35% of the soluble Cd to be transformed to Cd bound by organic matter (Figs 3(a) and 3(b)). At pH 7, 40–55% of the Cd was transformed to immobile forms. However, at pH 7, the soluble Cd was slightly greater than predicted and represented as much as 20–30% of the added Cd. The increase in soluble form of Cd can possibly be attributed to the dissolution of organic matter at higher pH values thereby releasing Cd into the soil solution (Kuo and Baker, 1980).

When the siliceous sand was amended with the lateritic podzolic soil, most of the Cd determined and that predicted in each of the forms were more or less similar at pH 4. At pH 7, the soluble Cd was less than that predicted and the exchangeable Cd was slightly greater than that predicted (Table 2). It appears that the majority of soluble Cd transformed into exchangeable forms at higher pH values (Figs 2(a) and 2(b)). These changes would not significantly affect the leachability or availability of Cd. However, a slight increase in Cd bound to organic matter and that in the residual fraction at pH 7 was observed which could be attributed to an increase in the number of adsorption sites due to the development of pH dependent adsorption sites on organic matter and on the edges of kaolinite (Bolland *et al.*, 1976; Lim *et al.*, 1980).

The results obtained in this work suggest that the amendment of sandy soils to reduce the potential of Cd leaching or uptake by plants may be achieved by the addition of yellow earth (i.e. materials containing hydrous oxides) at neutral pH values or peaty sand (i.e. materials containing organic matter) at low pH values. However, the use of yellow earth at neutral pH values could cause the leaching of phosphorus because the soil's ability to retain phosphorus (being an anion) would be reduced (Barrow, 1982). To reduce the risk of phosphorus leaching when using an amendment

containing hydrous oxides at pH 7, it would be advisable to use a less soluble source of P (Weaver *et al.*, 1988) or smaller amounts of P fertilizer. A smaller application of fertilizer would mean smaller additions of Cd and ultimately more transformation of mobile forms to immobile forms as discussed earlier (i.e. 70% at 0·8 $\mu g\ g^{-1}$ versus 45% at 10 $\mu g\ g^{-1}$). Increasing the pH of a mixture would be an additional cost if the yellow earth had to be used for amending a sandy soil with a pH < 5·5.

The addition of organic matter, such as in peaty sand, appears to be an effective amending material for the acidic sandy soils examined in this work. Decreases in Cd availability under acidic conditions in the presence of organic matter have been reported previously (Tyler and McBride, 1982; Elliott *et al.*, 1986; Tiller, 1988). In another study conducted in New Zealand, the removal of organic matter from one of the soils reduces Cd adsorption by 50% (Kim and Fergusson, 1992). At neutral pH values there may be some dissolution of the organic matter resulting in a reduced effectiveness for Cd retention (Mann and Ritchie, 1993). Nevertheless this appears to be relatively small in relation to the proportion of added Cd transformed from plant available to unavailable forms.

CONCLUSIONS

The problem of Cd leaching or its availability to plants in sandy soils can be reduced by amending sandy soils with soils containing high amounts of hydrous oxides or organic matter.

A yellow earth (containing goethite) was the most effective at pH 7 in transforming mobile forms of Cd to immobile forms, whereas a peaty sand (containing organic matter) was more effective at pH 4. A lateritic podzolic soil (containing kaolinite) was partially effective at high pH values, but its ability to transform mobile forms to immobile forms was comparatively much less than the other two soils.

REFERENCES

Barrow, N. J. (1982). Possibility of using caustic residue from bauxite for improving the chemical and physical properties of sandy soils. *Aust. J. Agric. Res.*, **33**, 275–85.

Bolland, M. D. A., Posner, A. M. & Quirk, J. P. (1976). Surface charge on kaolinites in aqueous suspension. *Aust. J. Soil Res.*, **14**, 197–216.

Brummer, G. W. (1986). Heavy metal species, mobility and availability in soils. In *The Importance of Chemical "Speciation" in Environmental Processes*, ed. M. Bernhard, F. E. Brinckman & P. J. Sadlers. Springer-Verlag, Berlin, pp. 169–92.

Christensen, T. H. (1984). Cadmium soil sorption at low concentrations: II Reversibility effect of changes in solute composition, and effect of soil aging. *Water Air Soil Pollut.*, **21**, 105–14.

Cox, J. A., Slonawska, K., Gatchel, D. K. & Hiebert, A. B. (1984). Metal speciation by Donnan dialysis. *Anal. Chem.*, **56**, 650–3.

Elliott, H. A., Liberati, M. R. & Huang, C. P. (1986). Competitive adsorption of heavy metals by soils. *J. Environ. Qual.*, **15**, 214–19.

Emmerich, W. E., Lund, L. J., Page, A. L. & Chang, A. C. (1982). Movement of heavy metals in sewage sludge-treated soils. *J. Environ. Qual.*, **11**, 174–8.

FAO-UNESCO (1974). Soil map of the world. 1:5,000,000. Food and Agriculture Organization-United Nations Educational, Scientific and Cultural Organization, Paris.

Harrison, R. M., Laxe, D. P. H. & Wilson, S. J. (1981). Chemical associations of Pb, Cd, Cu and Zn in street dusts and roadside soils. *Environ. Sci. Technol.*, **15**, 1378–83.

Hickey, M. G. & Kittrick, J. A. (1984). Chemical partitioning of Cd, Ni and Zn in soils and sediments containing high levels of heavy metals. *J. Environ. Qual.*, **13**, 189–97.

Kim, N. D. & Fergusson, J. E. (1992). Adsorption of cadmium by an aquent New Zealand soil and its components. *Aust. J. Soil Res.*, **30**, 159–67.

Kuo, S. & Baker, A. S. (1980). Sorption of Cu, Zn and Cd by some acid soil. *Soil Sci. Soc. Amer. Proc.*, **44**, 969–74.

Lim, C. H., Jackson, M. L., Koons, R. D. & Helmke, P. A. (1980). Kaolins: sources of differences in cation-exchange capacities and cesium retention. *Clays Clay Miner.*, **28**, 223–9.

Mann, S. S. (1989). Cadmium in fertilizers and soils. PhD Prelim., University of Western Australia.

Mann, S. S. (1993). Forms of cadmium in soils of Western Australia. PhD Thesis, The University of Western Australia.

Mann, S. S. & Ritchie, G. S. P. (1993). The effect of pH on the forms of cadmium. *Aust. J. Soil Res.*, **31**, 255–70.

Neal, R. H. & Sposito, G. (1986). Effects of soluble organic matter and sewage sludge amendments on Cd sorption by soils at low Cd concentrations. *Soil Sci.*, **142**, 164–72.

Northcote, K. H. (1974). *A Factual Key for the Recognition of Australian Soils*, 3rd edn. Rellim Technical Publications, Glenside, South Australia.

Ozanne, P. G. & Shaw, T. C. (1967). Phosphate sorption by soils as a measure of the phosphate requirement for pasture growth. *Aust. J. Agric. Res.*, **18**, 601–12.

Soon, Y. K. & Bates, T. E. (1982). Chemical pools of Cd, Ni and Zn in polluted soils and some preliminary indications of their availability to plants. *J. Soil Sci.*, **33**, 477–88.

Sposito, G. & Page, A. L. (1985). Circulation of metals in the environment. In *Metal Ions in Biological Systems*, ed. H. Sigel. Marcel Dekker, New York, pp. 359–66.

Tacey, W. H., Ward, S. C. & Summers, K. J. (1984). Soil improvement with bauxite residue. *J. Agric. West. Aust.*, **25**, 92–3.

Tiller, K. G. (1988). Cadmium accumulation in the soil–plant system: an overview in relation to possible transfers to agricultural products. In *Cadmium Accumulations in Australian Agriculture*, ed. J. Simpson & B. Curnow. Australian Government Publishing Service, Canberra, No. 2, pp. 20–47.

Tyler, L. D. & McBride, M. B. (1982). Mobility and extractability of cadmium, copper, nickel and zinc in organic and mineral soil columns. *Soil Sci.*, **134**, 198–205.

Van Riemsdijk, W. H., De Wit, J. C. M., Nederlof, M. M. & Koopal, L. K. (1990). Physico-chemical models for metal ion behaviour in soil. In *Contaminated Soil '90', Vol. 1*, ed. F. Arendt, M. Hinsenveld & V. Brink. Kluwer Academic Publishers, Karlsruhe, pp. 359–66.

Verloo, M. & Willaert, G. (1990). Direct and indirect effects of fertilization practices on heavy metals in plants and soil. In *Fertilization and the Environment*, ed. R. Merckx, H. Vereecken & K. Vlassak. Leuven University Press, Leuven, pp. 79–87.

Vlahos, S., Summers, K. J., Bell, D. T. & Gilkes, R. J. (1989). Reducing phosphorus leaching from sandy soils with red mud bauxite processing residues. *Aust. J. Soil Res.*, **27**, 651–62.

Weaver, D. M., Ritchie, G. S. P., Anderson, G. C. & Deeley, D. M. (1988). Phosphorus leaching in sandy soils: I Short-term effects of fertilizer applications and environmental conditions. *Aust. J. Soil Res.*, **26**, 177–90.

Williams, C. H. & David, D. J. (1973). The effect of superphosphate on the cadmium content of soils and plants. *Aust. J. Soil Res.*, **11**, 43–56.